THE ROLE OF SURFACE FORCES IN FRACTURE

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ABSTRACT

The role of surface forces in fracture is considered by incorporating the contribution of the adhesive forces between the crack walls into the net mechanical driving force. It is shown that attractive surface forces lead to a threshold stress intensity below which a crack will heal. In addition, the surface forces modify the kinetics of slow crack growth. Crack growth may provide an alternative experimental method for measuring fundamental surface forces.

I. INTRODUCTION

The central notion behind the present work is that surfaces forces acting between the walls of a crack behind the tip contribute to the overall balance of forces acting to drive the crack. These forces must be taken into account in any comprehensive description of fracture. It is convenient then to consider a crack to be under the influence of two distinct driving forces, one a crack advance force due to the applied stress and the other a crack closure force

From an historical perspective, the neglect of surface forces when considering the fracture process is understandable. In the majority of fracture configurations considered in the past emphasis has been placed on the conditions for crack growth, in particular unstable crack growth. Under such conditions the crack driving force provided by the applied stress swamps any contributions from surface forces. In some fracture configurations, for instance in the de-adhesion of an interface, where surface forces might be expected to exert a dominant influence, the fracture mechanics have not been well characterized: this despite the extensive work in the last fifteen years (1-5) on the adhesion of spheres to flat surfaces (a geometry that has a direct correspondence, for elasticity analysis, to that of a mode I crack, as was pointed out in 1939 by Westergaard, 6). Perhaps more importantly, however, was that until the last decade or so there were few direct measurements of the surface forces, especially down to distances of the order of atomic spacings. The best that could be done was to resort to values of the empirically determined van der Waals forces from the colloid science literature, values that different workers had difficulty reproducing to within an order of magnitude. However, the incredibly delicate experiments using crossed mica cylinders first carried out by Tabor and Winterton (7) and subsequently developed to a higher level of sophistication by Israelachvili, with Tabor (8) and with a variety of co-workers in Australia (9-12), have transformed our understanding of surface forces by providing precise, direct measurements. The theory of surface forces has also been significantly advanced in the last two decades. In particular, the work of the Russian group under Lifshitz (13) extended the quantum electrodynamics treatment of long range Van der Waals-dispersion forces to the pertinent case of parallel bodies separated by an intermediary phase. In addition, a number of groups (14-16) have demonstrated how these theories could be applied to problems in cell biology, wetting phenomena and colloid science.

As a result of these advances we are now in a position to consider the role that surface forces might have on the fracture process. We might anticipate surface force effects to be significant in view of the remarkably small crack opening displacements that characterize brittle solids, eg figure 1. Our purpose in this paper is to explore these effects. We shall be focussing on van der Waals forces because of their amenability to analytical description, but the underlying principles are expected to embrace other types of surface forces.

II. FORCES ACTING ON A CRACK

Our focus in this section is on the forces that may act on a crack and which must be taken into account in establishing a force balance at the crack tip. We deal specifically with physical forces as distinct from any chemical forces that may occur at the crack-tip itself as a result of bond-rupturing reactions. For the purposes of calculating stress intensity factors and relating to elasticity equations later we use continuum descriptions of the force distributions. We also assume that a fluid phase wets the crack along the walls and is connected to an external reservoir. These assumptions allow us to describe the surface force distributions in terms of interfacial stresses and, ultimately, of interfacial energies.

The principal force that can be applied to the crack is, of course, the applied stress intensity, an experimental variable dependent only on the loading geometry and load itself. The surface forces augment this force. Derjaguin (17) refers to the net effect of the surface forces as a disjoining pressure, Π. We shall simply regard this pressure as a distributed normal stress, $\Pi(x)$, at the interface, but (contrary to convention in colloid chemistry), adopting a positive sign to designate a closing stress.

A number of specific force contributions (17,18) to the total disjoining pressure can be identified: the van der Waals dispersion force, Π_D; electrical double layer forces, Π_{EDL}; forces due to hydrogen bonding in the phase between the crack walls, Π_{HB} ; forces due to preferential solute adsorption on the crack walls, Π_{AD} ; electrostatic forces, Π_E; forces due to the structure of the liquid, Π_{ST}. Since these forces are independent of one another, their individual contributions are additive and can be expressed as:

$$\Pi = \Pi_D + \Pi_{EDL} + \Pi_{HB} + \Pi_{AD} + \Pi_E + \Pi_{ST} \qquad [1]$$

Little is known about these terms with the exception of the dispersion and possibly also electrical double layer forces. These two figure importantly in the well-known DLVO theory (17,19,20) of colloidal stability, but as indicated earlier even these were not experimentally accessible until the crossed cylinder measurements. Also, the region of interest to the colloid science community was the long range, out to distances of microns rather than those pertinent to fracture here, namely less than 100 nm. The theoretical framework of Dzyaloshinskii et al. (13) and the subsequent work of Parsegian, Ninham and Gingell (14-16) enables precise calculation of the dispersion force to be made from optical constants of the materials. Specifically, the van der Waals dispersion force for two slabs of a given phase separated by a second phase of thickness, d, can be expressed as:

$$\Pi_D = \frac{\hbar}{16\pi^2 d^3} \int_0^\infty [\frac{\varepsilon_\alpha(i\zeta) - \varepsilon_\beta(i\zeta)}{\varepsilon_\alpha(i\zeta) + \varepsilon_\beta(i\zeta)}]^2 d\zeta$$

where $\varepsilon(i\zeta)$ are the dielectric permeabilities of the phases involved and ζ is a dummy variable. This may be re-written as:

$$\Pi_D = \frac{H}{6\pi d^3} \qquad [2]$$

where H is conventionally referred to as the Hamaker "constant". This equation has the form long familiar to the colloid science community. The difference is that the Hamaker "constant" is now a predictable quantity dependent only on the dispersion properties of the phases. The value of the Hamaker constant for most ceramic systems is of the order of $1 - 100\,kT$, namely $10^{-21} - 10^{-19}\,J$. We may note that if we define the van der Waals interaction energy as the work, $2\gamma_D$, to separate the two walls from an initial separation d_o to ∞ we obtain:
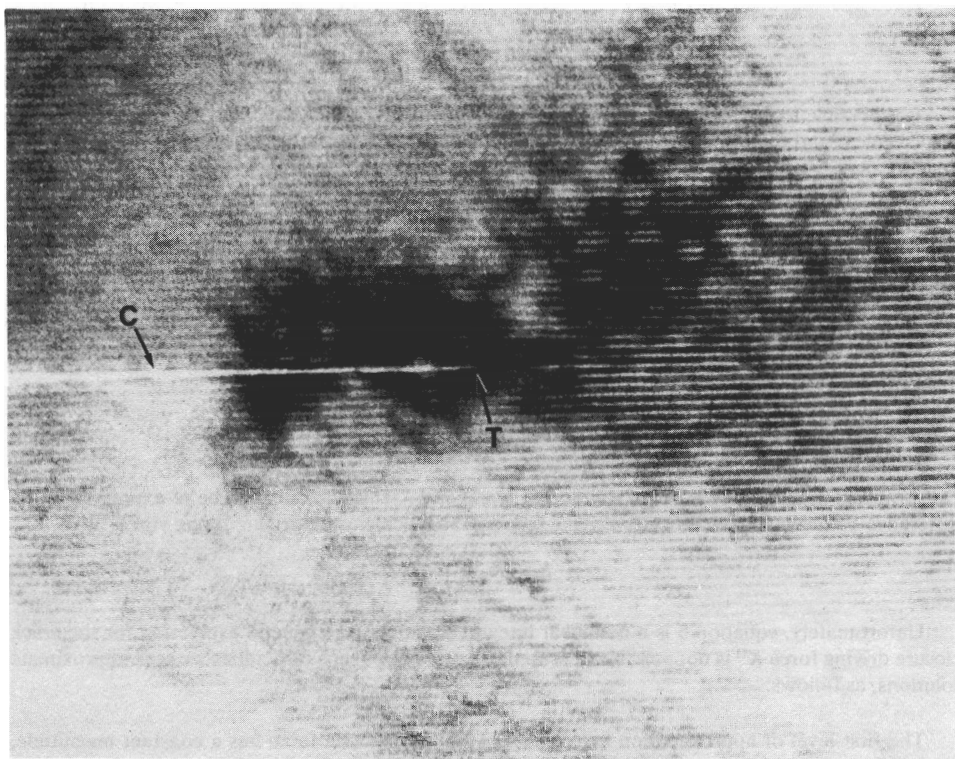
Figure 1.   A high resolution transmission electron micrograph of a crack-tip region in a magnesium Sialon material. The crack, C, is in a loaded state as evidenced by the diffraction contrast around the crack-tip, T. The lattice fringes correspond to the lattice spacing of the material.

$$2\gamma_D = \frac{H}{12\pi d_o^2} \tag{3}$$

III. FORCE BALANCE AND NET CRACK DRIVING FORCE

Given the form of the forces acting on a crack the next step is to calculate the effect they have on the crack driving force. This can perhaps be most usefully done through the sequence of thought experiments sketched schematically in figure 2 . Following the spirit of elasticity theory we introduce a narrow slit of length, 2c, by cutting the bonds across the slit. In the second step, a uniform external stress, σ_z, is applied normal to the plane of the slit, and this has the effect of opening the slit to form a crack. From elasticity theory[1] the opening of the crack can be represented (within the confines of the linear, continuum approximation) as an elliptical cavity:

$$u(x) = \frac{2K}{E\sqrt{\pi c}}\sqrt{c^2 - x^2} \tag{4}$$

where E is Young's modulus and K is the stress intensity factor. In the third step the interfacial forces are applied to the walls of the crack. The final form of the crack shape will be considered later but one pertinent feature may be singled out here. In general, the magnitude of $\Pi(u)$ is greater the smaller

Plane stress solutions; plane strain solutions can be obtained by replacing E by $\frac{E}{(1 - \nu^2)}$, where ν is Poisson's ratio.

the crack opening, u, so the effect of the surface forces will be more strongly felt as we approach the tip.

It is possible to use a Green's function approach to calculate the details of both the crack opening displacement and the net crack driving force (21). For an embedded penny crack the crack opening displacement is modified by the presence of the surface forces to:

$$u(x) = \frac{4}{\pi E} \int_x^c \frac{s}{\sqrt{s^2 - x^2}} \int_0^s [\sigma_\infty - \Pi(t)] \frac{t}{\sqrt{s^2 - t^2}} \, dt \, ds \qquad [5]$$

where s and t are dummy coordinates. In turn the net stress intensity factor is given by

$$K = \frac{2}{\sqrt{\pi c}} \int_0^c [\sigma_\infty - \Pi(x)] \frac{x \, dx}{\sqrt{c^2 - x^2}} \qquad [6]$$

Our principal interest here is in the solution of equation 6. This equation can be re-expressed as the difference between a crack advance driving force and a crack closure driving force, viz:

$$K = K_\infty - K^\Pi \qquad [7]$$

Unfortunately, equation 5 is a nonlinear integral equation, so a general expression for the crack closure driving force K^Π is not possible at present. In the face of such difficulties we seek approximate solutions, as follows:

The first level of approximation is to consider that the surface force has a constant magnitude, Π, and acts over a finite range, $u^\times$. This approximation is in the spirit of the Barenblatt cohesive zone (22). We define a threshold stress intensity factor, $K_\infty = K_{TH}^\Pi$ at $K = 0$ in equation 7, whence equation 6 reduces to:

$$K_{TH}^\Pi = \sqrt{E \Pi u^\times} = \sqrt{E \gamma_i} \qquad [8]$$

where γ_i defines the interfacial energy.

The next level of approximation is to assume that the crack shape is determined by the net stress intensity factor, as in equation 4. The shape fixes the magnitude of the interfacial forces. Then equations 4, 6 and 7 may be combined to give, for any general stress-separation function, $\Pi(u)$,

$$K = K_\infty - \frac{E \gamma_i}{K} \qquad [9]$$

where $\gamma_i = \int_0^{u^\times} \Pi(u) \, du$. The threshold condition is $K = K_\infty = K_{TH}$ which gives:

$$K_{TH} = 2\sqrt{E \gamma_i} \qquad [10]$$

The third level of approximation is a first order perturbation solution in which it is assumed (as in the thought experiment of figure 2) that the surface forces perturb the shape imposed by the applied stress. Thus far a solution has only been obtained for the van der Waals force function equation 2 (putting $d = 2u$). This solution is achieved by substituting equations 2 and 4 into 5 and then in turn into equation 6. The details of the calculations are beyond the scope of this contribution and will be published elsewhere (Clarke and Liniger, 23). They lead to an exact expression for the threshold stress intensity given by:

$$K_{TH}^D = \sqrt{\frac{HE}{12\pi d_0^2}} = \sqrt{2 E \gamma_D} \qquad [11]$$

(a)

2c

(b)

σ_∞

x

(c)

σ_∞
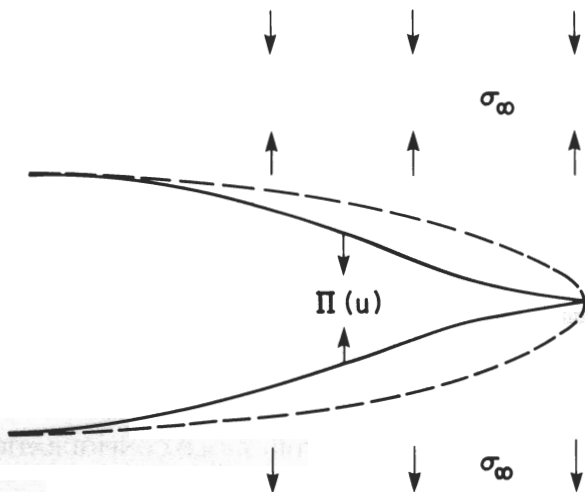
Π (u)

σ_∞
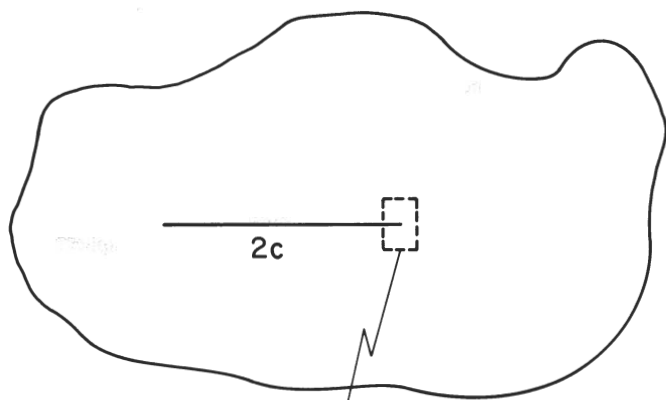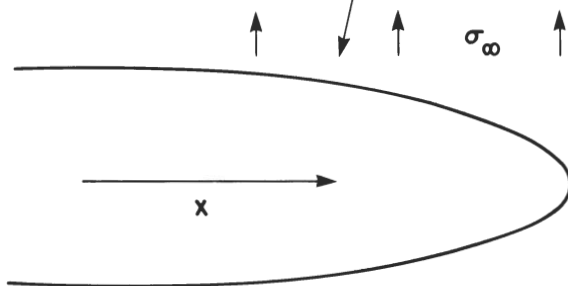
Figure 2.   Schematic diagram of the operations used to evaluate the displacements and stress
intensity factors for a crack subject to an applied stress and surface forces
between the walls of the crack.

In this region the solution to the displacement equation 5 shows that the crack walls "pinch down" into a cusp at the tip (figure 2c), in the manner of a Barenblatt cohesive zone, marking the onset of crack closure and retraction.

There is an implied equivalence between the surface force terms and corresponding interfacial energies in equations 8, 10 and 11 which bears further elaboration here. In the classic Griffith description (24) the condition for crack equilibrium is met when the rate of dissipation of mechanical energy just balances the rate of increase of surface (or interface) energy. In terms of fracture mechanics parlance this balance is expressible as:

$$K_c = \sqrt{2 E \gamma} \qquad [12]$$

It will be seen that if we identify γ in equation 12 with γ_D in equation 11 our third solution above represents a true Griffith equilibrium configuration, $K_c = K_{Th}^D$, in the sense that at $K > K_c$ the crack will advance and at $K < K_c$ will retract. We shall explore the implications of this further in the following section. Note also that the identity between equations 11 and 12 means that the first and second approximations in equations 8 and 10 must respectively underestimate and overestimate the threshold stress intensity factor.

Typically, van der Waals interaction energies fall in the range 10 to 100 $mJ.m^{-2}$. More exact estimates, using published values of Hamaker constants in equation 3, are listed in Table I.

TABLE I

DISPERSION FORCE CONTRIBUTION
TO INTERFACIAL ENERGY

Material System	Hamaker Constant 10^{-21} J	Interfacial Energy $mJ.m^{-2}$
Mica-Air-Mica	100	48
Mica-Water-Mica	22	10
Silica-Air-Silica	65	31
Silica-Water-Silica	8.3	4
Quartz-Air-Quartz	88	42
Quartz-Water-Quartz	17	8
Alumina-Air-Alumina	156	74
Alumina-Water-Alumina	53	25

IV. CRACK HEALING IN RELATION TO THRESHOLD CONFIGURATIONS

The physical significance of the threshold stress intensity factor is that it corresponds to the driving force below which a crack will retract and heal. There is ample evidence in the literature that healing can occur in highly brittle solids, even in the presence of chemical environments (25). Perhaps the most extensive review of the healing literature is given in an article by Case et al.(26) Particularly dramatic pictorial evidence for crack reversibility is shown by the beautiful electron microscopy studies of Hockey (27).

Although crack healing in glass (25) and alumina (27) is well documented, one of the best materials in which to observe the healing effect is mica, by virtue of its near molecularly smooth cleavage

(28). We have recently begun to use this material in an investigation of healing. Figure 3 is an example of muscovite mica cleaved in air. In figure 3a a wedge has been inserted into a flake, causing a crack to propagate to an equilibrium position. The open crack is rendered visible by virtue of the Fizeau fringe pattern. Figure 3b shows the same field after partial withdrawal of the wedge. The original front has clearly retracted. A spurious particle has become trapped at the interface in this second frame, leaving a residual penny crack within the otherwise totally re-adhered region. On re-inserting the wedge the configuration in figure 3a is once more attained. This experiment can be carried out in different environments, to determine the chemical dependence of the interfacial energy (28). Thus cyclic loading experiments in the threshold region have the potential for providing quantitative information on fundamental surface forces.

In most of our discussions here it has been tacitly assumed that the interfacial stresses will be attractive. This need not be so. There are indications that many of the force types in equation 1 will be repulsive. Electrical double layer forces are of this kind. A net repulsive force corresponds to a negative interfacial energy. It is evident from equations 8,10 and 11 that the threshold stress intensity factor for this case becomes imaginary. One can show (e.g. from equation 9) in such a case that a net force will persist on the crack even at zero externally applied loading.

V. SURFACE FORCES AND SLOW CRACK GROWTH

The influence of surface forces are expected to extend beyond equilibrium fracture properties, to the well known phenomenon of chemically-assisted, rate-dependent crack growth. Quantitatively, one characterizes this phenomenon by a crack velocity function $v(K)$, which depends on the material-environment system but is always monotonically increasing. Most of the velocity studies have been carried out on silicate glasses, although the rate effect has been demonstrated in a wide range of brittle materials. The relevance of such studies to surface forces is that the velocity functions appear to exhibit zero velocity cut-offs at low K values (29) suggestive of exactly the kind of threshold behavior described above. The question arises: if surface forces are indeed responsible for the threshold at $K = K_{TH}$, what effects do they have on the $v(K)$ function at $K > K_{TH}$?

The key to the answer to this question lies in the realization that it is the net stress intensity factor K at the crack tip which determines the velocity function, whereas in an experiment we actually measure the applied stress intensity factor K_∞; K and K_∞ are of course connected via K^{Π} in equation 7 where K^{Π} may itself be a function of K. Thus given an intrinsic velocity function $v(K)$, we may solve for $v(K_\infty)$ for any specified surface force state (ie K_{TH}). Calculations of this kind have been made in the spirit of the approximations embodied in equation 9, and are presented elsewhere (30). It becomes apparent that, in addition to the imposition of a threshold, surface forces can manifest themselves strongly as shifts in the entire crack velocity curve. Such shifts have been widely reported in the glass fracture literature, particularly as a result of variations in environmental solution pH (Wiederhorn and Johnson, 31).

It is of some interest to investigate the threshold itself a little more quantitatively. Recent data from indentation studies (32) give $K_{TH} \simeq 0.1$ $MPa.m^{1/2}$ for soda-lime glass in water. Taking $E = 70$ GPa we evaluate $\gamma_i \simeq 70$ $mJ.m^{-2}$ This value is considerably larger than that due solely to van der Waals dispersion forces (Table I-- fused silica data). This suggests that we must consider the other force terms in equation 1. For aqueous environments we might pay particular attention to the hydrogen bonding and structural forces. Water is a strongly associated liquid and appears to have a long-range structure, quite unlike that of other liquids. The long range structure has been measured directly in the sensitive crossed cylinder experiments of Pashley and Israelachvili (10). Furthermore, the chemical interaction between the silicates and the water not only alters the glass but also alters the properties of the water itself (33). Perhaps most striking is the fact that silicates and water react to form what was once termed "anomalous water", a phase having anomalous transport properties relative to those of water itself (17). Although initial claims that anomalous water may constitute a new liquid phase of water were subsequently discounted, the experiments substantiated the picture of some structural interaction between the liquid phase and the adjacent silica surface. The experiments in which the effect was particularly marked were performed with the water trapped in narrow capillaries of silica, a geometry not dissimilar to that of a crack interface. In considering these possibilities it is well to be aware of the extremely small crack wall displacements which typify highly brittle solids (eg. figure 1), a confinement which can only be enhanced by the Barenblatt-type cusping re-
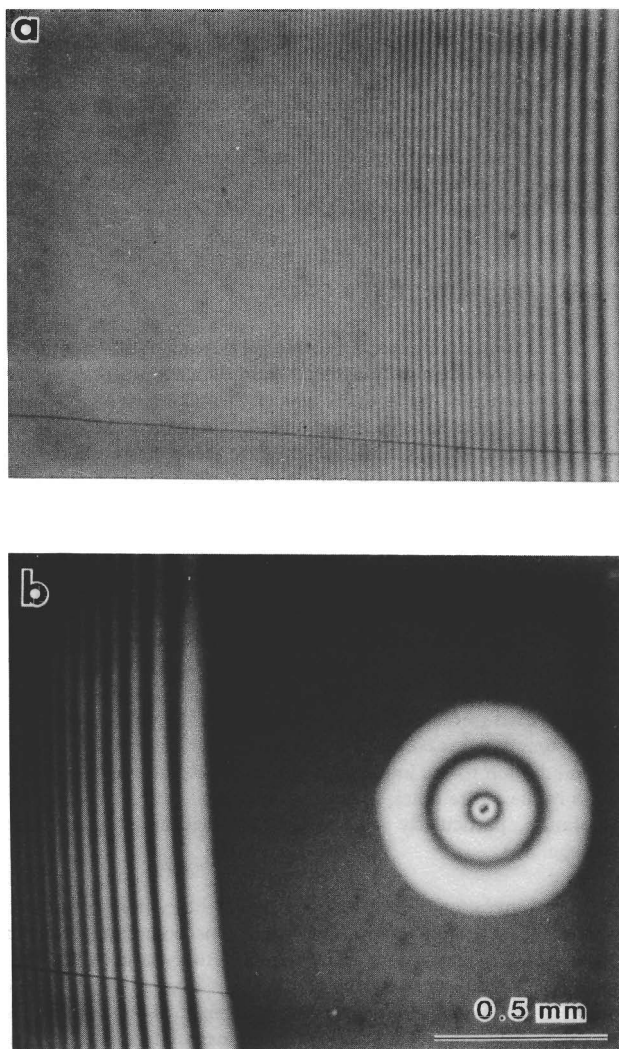
Figure 3. A crack in muscovite mica formed in air by the insertion of a wedge into the edge of the crystal. The wedge has been fully inserted in (a) and then partially withdrawn in (b).

ferred to earlier. In this picture it may be more proper to regard the interface in the near-tip region as akin to a grain boundary rather than an open cavity (18). Such constriction could well determine in a steric manner those ions which can enter the critical reaction zone at the crack tip (Michalske and Bunker, 34).

VI. CLOSING REMARKS

We have mentioned the crossed mica cylinder experiments as the only existing direct way of measuring surfaces forces down to distances close to the interatomic spacing. Unfortunately, as presently implemented, this method is restricted to mica (or other such conformable materials having atomically flat surfaces). The recognition that surface forces may have a predictable effect on fracture, and in particular on a definable threshold behavior, opens up an entirely fresh avenue for measuring surface forces, namely via the fracture process itself. The study of fracture has been preoccupied with characterizing the conditions under which a material might fail. Now, fracture might well prove to be a useful tool for measuring some of the fundamental forces acting in nature, having direct relevance to fields as disparate as colloid science, wetting phenomenon, ceramic processing and cell biology. It is anticipated that fracture in brittle materials such as sapphire, mica and glass may prove to be especially suitable for such surface force measurements.

In summary we would emphasize the following points:

1. Surface forces acting between the walls of a crack, but behind the crack tip itself, provide a crack driving force which supplements that originating from an externally applied stress.

2. For the specific case in which the surface forces cause the opposing walls of a crack to be attracted to each other, the additional driving force acts as a crack closure force. When the crack advance force is balanced by the crack closure force, a condition of zero net driving force on the crack exists. This condition is a measure of the surface forces acting on the crack. The threshold stress intensity is also pertinent to kinetically controlled slow crack growth since it is the value at which the crack growth rate will go to zero.

3. The specific case of van der Waals dispersion force acting on a crack is shown to lead to a threshold stress intensity whose magnitude is proportional to the square root of the Hamaker constant for the crack system.

4. For surface forces that are attractive, it is indicated that in the immediate vicinity of the crack-tip the crack is "pinched" down. This effect is more marked the closer the applied stress intensity is to the threshold.

5. For those cases in which the surface forces are repulsive in nature, no threshold stress intensity will exist, but rather the crack will exhibit nonzero crack velocity at zero applied driving force.

6. Particularly exciting is the prospect of using the fracture process itself, at small crack driving forces, to measure surface forces directly.

ACKNOWLEDGEMENTS

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